

ART. XV.—*Coorongite, a South Australian Elaterite.*

By ALEX. C. CUMMING.

(Communicated by PROFESSOR ORME MASSON, D.Sc.).

[Read 9th October, 1902.]

The name *Coorongite* was given many years ago to a peculiar substance found as a thin superficial deposit on the soil in the *Coorong* district of South Australia. A small sample was recently sent to the Chemical Laboratory of the University of Melbourne, and has been examined by me, under Professor Masson's direction, with results to be described in the sequel.

Previous Accounts.—*Coorongite* is briefly described by Krausé (Mineralogy, p. 138), and by G. C. Morris (Proc. Acad. Nat. Sci. Philadelphia, 131, 1877), and references have been found elsewhere; but by far the best and fullest account of it that I have been able to find is contained in a paper by J. R. Jackson, published in the *Pharmaceutical Journal* of 1872 (pp. 763 and 785). From this paper it appears that *Coorongite* had, since its discovery in 1865, excited a good deal of interest both in Australia and in England, and that the question of its true nature and probable origin had been the subject of considerable discussion. Very different views were expressed, some regarding the substance as a bituminous hydrocarbon mineral, others believing it to be of vegetable origin. These discussions of thirty years ago appear to have been forgotten, and within the last year attention has been directed afresh to the same questions, still unsettled, by newspaper accounts of quests for mineral oil in the district where *Coorongite* occurs. Jackson's paper was not known to me till after I had done the work to be described. My results are, in the main, corroborative of those he records and quotes from other observers, but additional information has been gained as to the chemical nature of the material.

Description of Coorongite.—My specimens were in sheets varying from one-tenth to one centimetre in thickness. The substance varied in colour on the surface from greyish-black to black, but

was uniformly black internally. It was soft, flexible, and elastic, resembling caoutchouc; one surface, probably the upper, was hard, black, and sponge-like; it contained a considerable quantity of sand and some vegetable fibres; it burnt readily with a white flame, melting before the flame, and giving, especially when extinguished, a characteristic odour, quite distinct from that from hydrocarbon minerals, and suggestive of burning animal or vegetable fats. Jackson gives the following analysis of Coorongite by Dr. A. J. Bernays:—

Moisture	0.4682
Carbon	64.73
Hydrogen	11.63
Ash	1.79
Fixed carbon	1.005
Oxygen and unest.	20.3768
				<hr/>
				100.0000

The substance is insoluble in water and alcohol, and only partially soluble in carbon bisulphide, ether, chloroform, turpentine, benzene and toluene, giving bright yellow solutions. This confirms observations of G. Francis, quoted by Jackson. On evaporation of the solvent a soluble body of low melting point is obtained, the Coorongite being thus separated into this body, and a friable insoluble residue.

Separation into two constituents by extraction with Carbon Bisulphide.—100 grms. were cut up into small pieces and subjected to successive extractions with carbon bisulphide in a Soxhlet's extractor. After the first extraction the residue, which was quite friable, was rubbed to powder before adding fresh solvent. The product of each extraction was separately examined after evaporating off the carbon bisulphide. The results are shown in the following table:—

	Time of Extraction.			Weight of Extract.
1st Extraction	...	7 hours	...	20.80 grms.
2nd ,,	...	12 ,,	...	2.78 ,,
3rd ,,	...	16 ,,16 ,,
4th ,,	...	18 ,,05 ,,
				<hr/>
				53 hours.
				<hr/>
				23.79 grms.

Thus the sample yielded nearly 24 per cent. of the soluble constituent. As the residue was found to contain from 30 to 40 per cent. of sand and other mineral matter, the soluble constituent formed about one-third, and the insoluble constituent about two-thirds of the organic material. The results of the later extractions show that separation was complete.

The Soluble Constituent.—This is a clear, yellow, translucent, wax-like solid. Softens enough to flow if kept at 35°, and is quite fluid at 42°. Heated in an oil bath it decomposed above 225°, yielding a little black distillate and a tar-like solid residue.

It dissolves readily, and in all proportions, in benzene, ether, toluene, chloroform, and carbon bisulphide, and is insoluble in water, methyl alcohol and ethyl alcohol.

The composition was obtained by combustion with cupric oxide in a current of oxygen. The results agree closely with the figures calculated for the formula $C_{10}H_{18}O$.

	I.	II.	III.	Mean.	Calculated for $C_{10}H_{18}O$
Carbon - - -	77.86	77.94	77.92	77.91	77.92
Hydrogen - - -	11.97	11.87	11.93	11.92	11.69
Oxygen (by difference)-	10.17	10.19	10.15	10.17	10.39

As the molecular weight could not be got by vapour density measurement, recourse was had to the freezing point method, using benzene as solvent. The benzene used was specially purified and had the freezing point 5.33° cor. Ice and water were used for freezing and five observations were made at each temperature. The constant K for the benzene was determined by experiment with naphthalene, which gave a value of 5390.

1.080 grms. of the substance dissolved in 30.0 grms. benzene lowered the freezing point .080°.

Using the formula

$$M = K \frac{S}{\Delta L}$$

where M = molecular wt., K = a constant (5390 in this case) Δ = the depression produced, and L = weight of solvent, these figures indicate a molecular weight of 2425. The formula $(C_{10}H_{18}O)_x$ requires a molecular weight of 154, or some multiple thereof; and it would therefore appear that the value of x in benzene solution is 16 ($M = 2464$), or, in other words the

soluble constituent of Coorongite is $(C_{10}H_{18}O)_{16}$ in benzene solution.

It is well known, however, that organic oxygen derivatives of the alcohol and acid kind are given to association in benzene solution, though they have simple molecules in other solvents, and that the molecular weight of a substance in benzene solution is often twice as great as the normal.

Observations were therefore made on the boiling point of an ether solution of the substance, using ether purified by distillation from sodium immediately before use.

The whole of the ether (about a litre) distilled at 34.2° , but the first and last portions were rejected.

The boiling point was raised $.100^\circ$ by the addition of 1.370 grms. of the material to 24.1 grms. of the ether, which by the formula

$$M = K \frac{S}{\Delta L}$$

where K for ether = 2100, S and Δ have values given above and $L = 23.9$ (allowing for vapour, etc.), gives the approximate value 1204 for the molecular weight, which is within the error of experiment, half the value obtained in benzene solution. In these experiments, Beckmann's freezing point and boiling point apparatus were used with thermometers divided into hundredths of one degree C. and capable of being read by eye to $.002^\circ$.

The results obtained indicate that the soluble constituent of Coorongite is $(C_{10}H_{18}O)_x$ and that $x=8$ in ethereal solution and 16 in benzene solution; x may, of course, have other values under other conditions.

Only an incomplete examination of the chemical properties of this substance has been made as yet. It is unacted on by acids except strong H_2SO_4 , which chars it.

It combines with bromine, forming a black, viscous, sticky, semisolid, readily soluble in carbon bisulphide and ether, but which has not yet been investigated.

It oxidises readily, as will be shown later. Attempts to saponify it led to negative results, though it is stated by Jackson to be saponifiable.

The Insoluble Constituent.—This was rubbed to a coarse powder during the extraction and resembled brown cork filings

mixed with much sand. Practically all the elasticity is lost during the carbon bisulphide extraction ; it is combustible, burning with a white luminous flame and melting before the flame ; when burning it gives the same odour, like that of a burning fat, which Coorongite itself gives. Analysis by combustion gave the following results for the organic matter :—

	I.	II.	Mean.	Calculated for $C_{10}H_{20}O_3$
Carbon - - -	64.16	64.28	64.22	3.836
Hydrogen - - -	10.54	10.50	10.52	10.64
Oxygen (by difference) -	25.30	25.22	25.26	25.53
	<hr/> 100.00	<hr/> 100.00	<hr/> 100.00	<hr/> 100.00

The amount of ash (principally sand) varied from 30 to 40 per cent. The figures for the organic part agree remarkably well with those calculated for $C_{10}H_{20}O_3$, seeing that the material has undergone no purification other than the treatment with carbon bisulphide. Its dark colour suggests that it contains traces of some more highly carbonaceous material, which would account for the slight discrepancy.

This constituent, unlike the soluble one, was found to be saponifiable by hot alcoholic caustic potash, a soluble soap being obtained which yielded an insoluble fatty body, on treatment with acid. This action has not yet been further examined.

Intermediate Oxidation Products.—The similarity of the formulae $C_{10}H_{18}O$ and $C_{10}H_{20}O_3$ suggest that the insoluble ingredient is derived from the soluble one by a natural change involving hydration and oxidation combined.

Observations made in the course of the examination tended to confirm this and to show that changes of this nature are readily brought about. In the following table are given the results of the combustions of three products obtained from portions of the soluble extract. No. I. was got by blowing air through the carbon bisulphide solution ; No. II. was formed during an attempt to extract some of the substance with methyl alcohol ; No. III. was obtained when trying to distil it in steam. They were separated as completely as possible from unaltered substance by centrifuging the mixture at a temperature high enough to keep the latter in a molten condition. These three substances had the appearance of the clear first constituent of the Coorongite,

but containing an opaque, yellowish, granular precipitate. They could not be separated by solubility in carbon bisulphide or ether, but a partial separation was effected by centrifuging.

For comparison, the mean results of the combustions of the soluble and insoluble constituents and the calculated values are again given. It is evident from the table that products I., II. and III. are incompletely oxidized mixtures.

	C.	H.	O (by diff.).
Calculated for $C_{10}H_{18}O$ -	77.92	11.69	10.39
Soluble constituent -	77.91	11.92	10.17
Product No. II. -	71.87	11.11	17.02
Product No. I. -	70.35	11.42	18.23
Product No. III. -	66.46	10.71	22.83
Insoluble constituent -	64.22	10.52	25.26
Calculated for $C_{10}H_{20}O_3$ -	63.83	10.64	25.53

The Ash.—The ash comprised about 25 per cent. of the sample on which this work was done, but in a latter specimen, since obtained from R. H. Walcott, Esq., F.G.S., of the National Museum, only 5.4 per cent. of ash was found. The analysis failed to show the presence of any phosphates, which would be expected if the Coorongite were of animal origin. The ash had the following composition:—

Silica	95.12
Aluminium and iron oxides	3.66
Calcium oxide	1.17
Sodium chloride	Trace
				<hr/> 99.95

Mr. D. J. Mahony kindly examined the mineral part of Coorongite, and found a number of species of typical fresh-water diatoms. Only a small part consisted of diatoms, the ash being mostly sand, and it is doubtful whether the occurrence of these diatoms is more than accidental.

Conclusions.—Coorongite has been shown to consist of two substances, one with the formula $(C_{10}H_{18}O)_x$, and the other $(C_{10}H_{20}O_3)_y$. The physical properties of the substance have earned it the name of Mineral Caoutchouc, and these formulae favour the idea that it is really related to caoutchouc, which has the formula $(C_{10}H_{16})_x$. Caoutchouc oxidizes readily, even taking

up oxygen from the air, and some of the substances connected with it, and with gutta percha have compositions and properties very similar to those of the two constituents of Coorongite. The formulae for these constituents are readily derivable from $C_{10}H_{16}$ by oxidation and hydration. However, for the present the nature of Coorongite must still be considered an open question, as much remains to be done in the further chemical investigation of its constituents.

BIBLIOGRAPHY OF COORONGITE.

- 1862. Phipson, T. L. *Geologist*, vol. v., p. 141.
- 1866-7. Ulrich, G. H. F. *Official Record of Intercolonial Exhibition*, pp. 91 and 168.
- 1872. Jackson, J. R. *The Pharmaceutical Journal and Transactions*, pp. 763 and 785.
- 1877. Morris, G. C. *Proc. Acad. Nat. Sciences, Philadelphia*, p. 131.
- 1892. Dana, J. D. *System of Mineralogy*, p. 1019.
- 1889. Roscoe and Schorlemmer. *Treatise on Chemistry*, vol. iii., pt. 5, p. 498.
- 1896. Krausé, F. M. *Introduction to the Study of Mineralogy for Australian Readers*, p. 138.
- 1896. Chester, A. H. *Dictionary of Names of Minerals*, p. 64.
- 1902. *Petroleum Prospecting in South Australia*. "The Argus," Melbourne, June 23rd, p. 8.